QUANTITATIVE SIMULTANEOUS MULTI-ELEMENT MICROPROBE ANALYSIS USING COMBINED WAVELENGTH- AND ENERGY-DISPERSIVE SYSTEMS

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QUANTITATIVE SIMULTANEOUS MULTI-ELEMENT MICROPROBE ANALYSIS

USING COMBINED WAVELENGTH- AND ENERGY-DISPERSIVE SYSTEMS

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ABSTRACT. A combined WDS-EDS system obviates the severe x-ray peak overlap problems encountered with Na, Mg, Al and Si common to pure EDS systems. By application of easily-measured empirical correction factors for pulse pile-up and peak overlaps which are normally observed in the analysis of silicate minerals, the accuracy of analysis is comparable with that expected for WDS electron microprobe analyses. The continuum backgrounds are subtracted from the spectra by a spline fitting technique based on integrated intensities between the peaks. The preprocessed data are then reduced to chemical analyses by existing data reduction programs.

Quantitative Simultaneous Multi-Element Microprobe Analysis Using Combined Wavelength- and Energy-Dispersive Systems

INTRODUCTION:

The accuracy of energy-dispersive spectrometry (EDS) has been reported to be inferior to wavelength-dispersive spectrometry (WDS) for the microprobe analysis of elements present at low (less than 2 wt.%) concentrations. [1] There are, however, several advantages to EDS analyses which have made it worthwhile to develop the system and technique so that, for at least a restricted compositions, the results approach the precision and accuracy of those of WDS.

The advantages of EDS are:

1. Many elements can be determined simultaneously. This is particularly important in the analysis of heterogeneous materials such as silicate crystals in lunar samples which have important compositional variations. Previous Analyses using three WDS spectrometers required the precise location and relocation of the analyzed points as several "passes" were made through the samples between sessions of re-tuning the spectrometers.

2. The time required to set up, run standards and perform analyses is considerably less than that required by computerized WDS. The latter technique presents two drawbacks not encountered in EDS:

a. the buildup of contamination spots may be come a problem during the long process of computerized WDS, and

b. the system is quite reliant on the mechanical relocation of the peak positions (the technique of peak-search using a computerized WDS cannot be efficaciously applied to elements in minor concentration

because low count rates result in inordinately long search times).

3. Many older electron microprobes cannot easily be outfitted with high-speed motor-driven spectrometers.

4. The use of EDS permits the simultaneous determination of background and peak intensities.

On the other hand, the low spectral resolution of EDS relative to that of WDS is a basic problem which must be solved before any such system is practical. In our system, we have made three provisions which ameliorate the effects of low EDS resolution:

1. The system has been set up for the analysis of one, rather broad class of samples - generally silicates.

2. Elements which fluoresce in the low-energy portion of the spectrum (i.e., Na, Mg and Al) are analyzed by WDS.

3. In cases in which complete resolution of the EDS spectrum cannot be achieved, the data are corrected using empirical, pre-determined overlap factors as described in a later section of this paper.

It should be noted that there is a more general approach to the solution of the problem of peak overlap.

Several methods of data reduction [2,3,4,5] have been proposed which involve the deconvolution of the EDS spectrum. This approach has two main operational advantages: it requires the collection and handling of an excessive amount of data and the computer time needed to perform spectrum stripping is often beyond a laboratory's means. An empiracal approach, while not as generally applicable, can be evolved which takes into account only those overlaps which are a problem in a narrow range of analyses. Within this range, this approach can give more accurate

results since corrections are based on parameters determined on that instrument on which the analyses are performed.

The EDS/WDS system described here has evolved with this analytical philosophy in mind: Sacrifice general applicability in order to obtain faster results with greater accuracy. Below we describe this system and the empirical corrections applied.

SYSTEM:

In Figure 1, the system is outlined in a block diagram.

The WDS portion, as presently configured, consists of two ADP crystals which are used for the analysis of magnesium and aluminum. Sodium is determined using an RAP crystal (the signal from each proportional detector is pre-amplified within the tank of the microprobe). The pulses are peaked in three pulse height analyzers, counted and fed into a data translator

The EDS system employs a Li-drifted Si crystal with a resolution of 180 eV as determined in situ. After amplification and pulse-shaping, the signal from this crystal is fed into an integrating multi-channel analyzer. A signal from a pulse generator (60 cps) is also provided to the MCA.

The selection of the MCA was based on its capability of integrating the counts in a variable number of optional pre-set ranges. This approach is considerably less expensive than providing a pulse-height analyzer/scaler combination for each eV-range, if more than three ranges are simultaneously recorded. Furthermore, a 1024-channel MCA has sufficient resolution in comparison to that provided by the detector crystal. In terms of eV/channel, integration over 10 channels of this MCA will yield approximately 90 percent of the counts under one spectral peak. The energy ranges over which the

integrations are performed are presented in Table 1.

The integrated intensities from the WDS and EDS, together with pulser, integrated beam current and time data are channeled through a data translater. These numerical data are printed on a hard copy and are punched onto paper tape. The paper tape can then be read directly onto a computer from a remote terminal for data manipulation.

PRE-CORRECTIONS AND DATA HANDLING:

Figure 2 illustrates the development of the spectrum, as it is "cleaned up" by the computer software.

1. Background Correction: In conventional microprobe analysis, backgrounds are generally determined by measuring the intensity at the characteristic wavelength used to analyze element M in a background standard which is devoid of element M but has approximately the same matrix as the sample to be analyzed. As the concentration of element M becomes lower, it becomes necessary to obtain "background" standards of increasingly greater purity and, at the same time, represent matrices closely analogous to the sample. In such cases, one often reverts to the technique of measuring background intensities on either side of the peak for both standards and samples. This procedure, however, is time-consuming and, if not performed accurately, can result in decreased precision because of the difficulties involved in relocating peak positions.

With the entire EDS spectrum available for analysis, it becomes possible to utilize regions between peaks to define the background spectrum for each sample and standard. The lower resolution of EDS might cause a peak to appear in a portion of the spectrum which is being employed for the determination of background. But once again we can rely on the fact that

we limit the applicability of our system and define background regions

which can be used for a somewhat restricted class of samples.

An attempt to fit the background curve to the equation:

$$A(E - E_c)^n \exp^{-\alpha E}$$

met with moderate success. The advantage of using such an equation is

clear: Only three measured points are required to define the curve.

Unfortunately, the equation can magnify the statistical variations in-

herent in the background intensities so that those measured points must

be known with inordinate precision.

Fitting the background curve to the data points by way of splines

was found to be more satisfactory. In this method, a smooth curve is fit

through three adjacent points but the curve is smoothed over all the points

in such a way that the slopes of adjacent curve segments at their inter-

sections are the same. Acceptable precision is obtained using six background

points, provided that the individual points (as determined by the number

of counts in each which is related to the number of channels integrated

for each point) have sufficient individual precision.

The spline-fit background correction was applied to spectra derived

from pure $MgSiO_3$ and a glass containing 2 weight percent FeO. After

background correction, the FeO-bearing sample had a peak intensity of 60

counts per second over the energy range used for Fe analysis while the

$MgSiO_3$ had only 1.5 c.p.s. It is quite likely that this comparison can

be improved by longer counts and better statistics.

2. Dead-Time Correction: The relative amount of time during which

the multi-channel analyzer is busy storing counts and consequently unable to

accept new counts is referred to as dead-time. This can be precisely

determined by feeding the MCA with an oscillating signal of known frequency. The counts observed in the rest of the spectrum can then be corrected by the value P_e/P_o where P_e and P_o are the expected and observed counts in the pulser channels, respectively. (It is, of course, necessary that P_o be the value observed <u>after</u> background correction and that the background near the pulser be quite accurately determined.)

3. <u>Pulse Pileup</u>: The advent of electronic pulse pileup rejection may obviate the need for this correction but without such a device, the inability of the MCA to distinguish between one pulse at energy E and two simultaneous pulses at energy E/2 resulted in a most serious problem. This was due to the fact that we generally analyze silicates (Si K_α = 1.74 KeV); but, at the same time, we wish to determine relatively small (ca. 1%) levels of potassium (K_α = 3.32 KeV). The pileup of the Si radiation at the K position, as shown in Figure 2 can thus be a major source of error.

An empirical correction was evolved to correct for pulse pileup. In this case, the correction is for the effect of Si K_α-radiation on K K_α. The method could equally be set up for other interferences. A series of standards (SiO_2, $MgSiO_3$, $CaAl_2Si_2O_7$, Mg_2SiO_4, etc.) which contained variable amounts of Si and no K were analyzed. The Si-radiation and the apparent K-radiation were background and dead-time correction. A second-order polynomial least squares fit to these points, in terms of:

$$K_{app} = aSi^2 + bSi + c$$

gave:

$$a = 7.41 \times 10^{-6}; \ b = 7.80 \times 10^{-4}; \ c = -1.99.$$

These parameters would undoubtedly have to be evaluated for every individual system.

4. <u>Overlap Corrections</u>: The overlaps discussed here were particular problems in our analyses, but, again, their correction may be regarded as exemplary of other corrections which might be applied. One advantage in performing these corrections, however, is that they are, in an absolute sense, very small

The EDS system is unable to distinguish between potassium K and calcium K_α. On the other hand, in order to obtain statistically significant counts, the energy regions of integration under the potassium and calcium K_α peaks are set quite close together. This can result in calcium K_α-counts "spilling over" into the potassium channels. Two correction factors were determined; one for the K K_β-effect on Ca K_α and the other for the Ca K_α-effect on K K_α. As before, this was accomplished by analyzing standards which contained one of these elements but not the other ($CaSiO_3$ and $KAlSi_2O_6$). The ratio of counts appearing in K K_α to the K K_β appearing in Ca K_α is .085. The ratio of counts in Ca K_α which spill over into K K_α is .0142.

SUMMARY:

Our efforts have been designed to produce an empiracal, practical and usable method for simultaneous quantitative analysis of several elements using the microprobe. Table 1, which is a comparison of a wet chemical analysis and the microprobe analysis, using the combined WDS/EDS system described here, substantiates the fact that we have achieved this purpose. The technique and correction factors, however, would certainly have to be modified if the method is to be used for other instrumentation and in different chemical matrices.
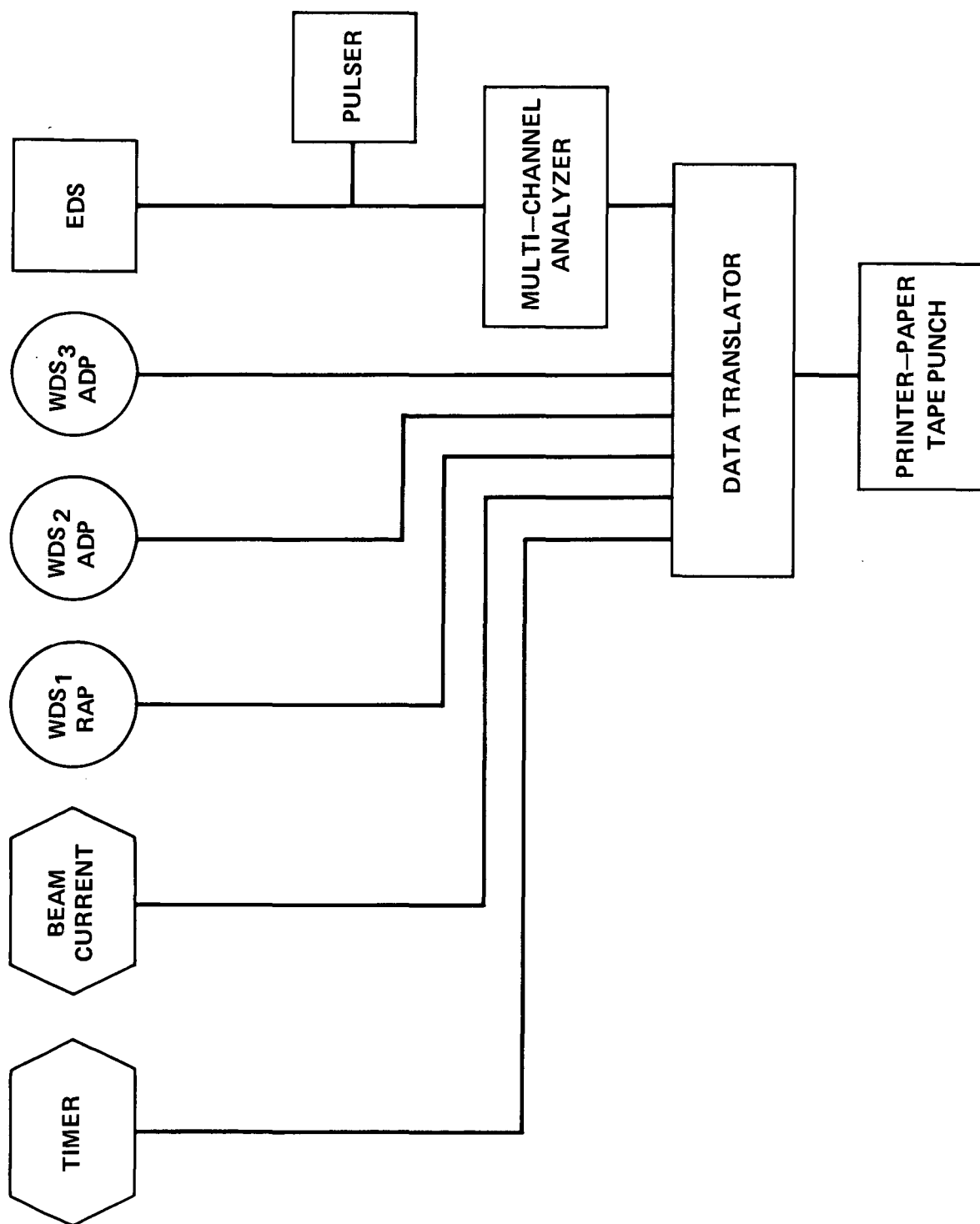
A more general treatment, utilizing simplfied spectrum stripping is being developed as a compromise between this empirical method and more complex deconvolution schemes. This, in combination with the ever-improving electronics ancillary to EDS-analysis may increase the precision and accuracy of these analyses still further. Even when modified by the inclusion of a pulse pileup rejector, the system will still take advantage of several of the elements described here, viz., internal background correction, dead-time correction and data compression.

At present, however, our experience indicates that the results of this combined system approach the quality of straightforward WDS analysis and, in addition, have several advantages over this and even computerized WDS systems.

FIGURE CAPTIONS

Figure 1 - Schematic of configuration of combined Energy Dispersive (EDS) and Wavelength Dispersive (WDS) system.

Figure 2 - Schematic representation of the modification of the EDS spectrum through the progressive corrections as described in text: 1) Original spectrum; 2) Background correction applied; 3) Dead-time correction applied (not increase in heights of all peaks); 4) Pulse pileup correction applied; 5) Correction of K K_α-intensity on the basis of Ca K_α-intensity; 6) Correction of Ca K_α-intensity on the basis of K K_α-intensity.
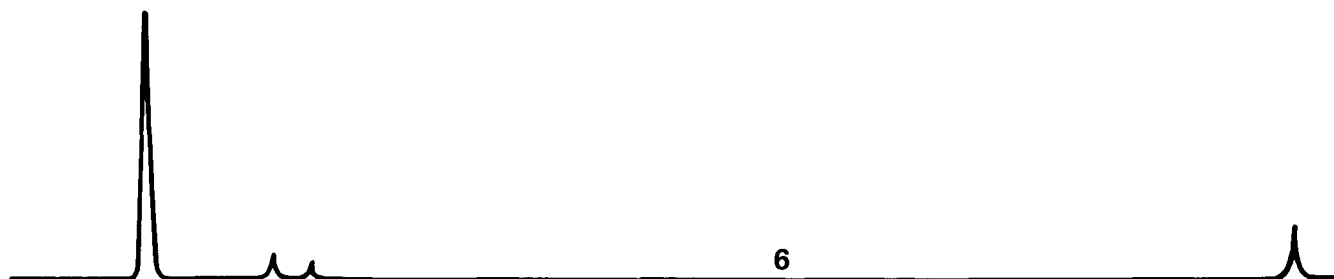
PULSER

EDS

MULTI-CHANNEL
ANALYZER

WDS 3
ADP

WDS 2
ADP

WDS 1
RAP

BEAM
CURRENT

TIMER

DATA TRANSLATOR

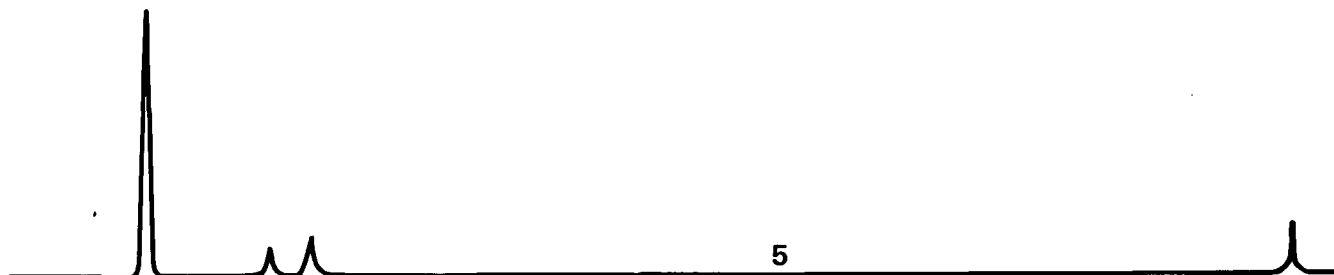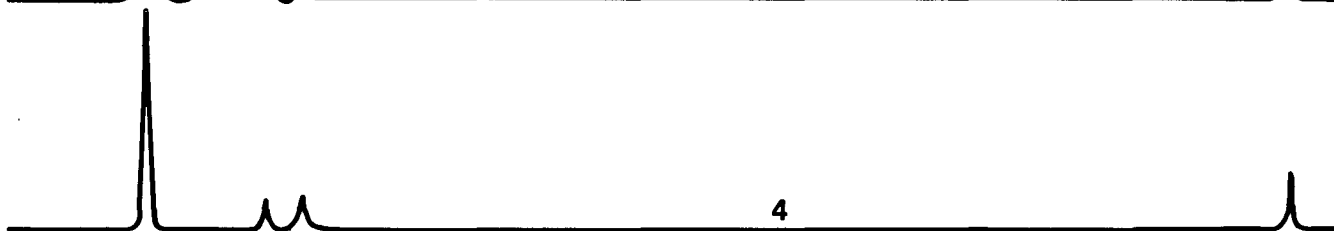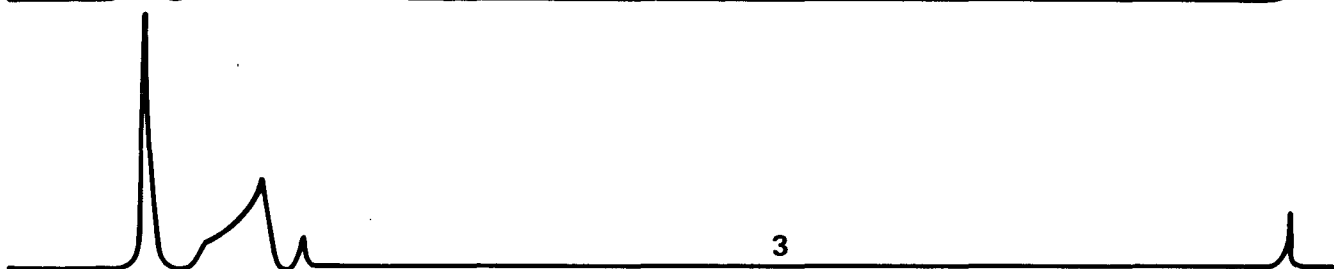PRINTER-PAPER
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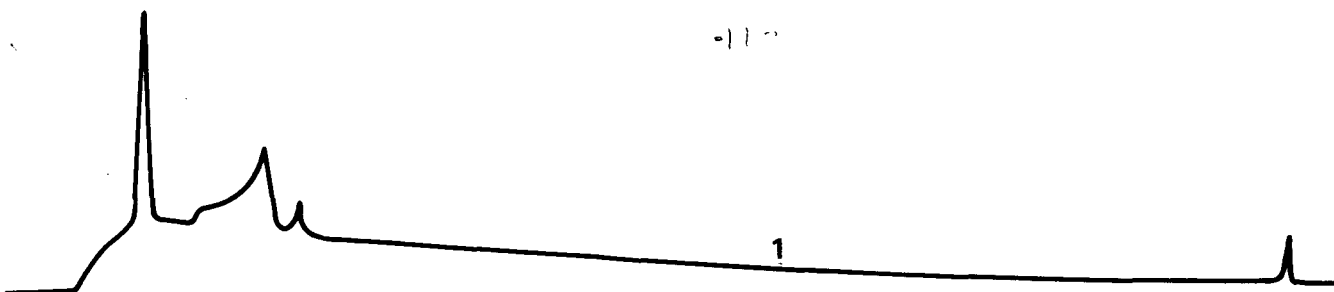
TABLE I

ENERGY RANGES AND IDENTIFICATION OF INTEGRATION REGIONS USED

Line*	Peak Position	Integration Range (KeV)
BK	-	.600 - .620
Si	1.74	1.68 - 1.86
BK	-	2.08 - 2.28
EB	-	2.64 - 2.84
K	3.32	3.20 - 3.40
Ca	3.68	3.58 - 3.78
BK	-	4.12 - 4.32
Ti	4.50	4.42 - 4.62
BK	-	5.04 - 5.24
Cr	5.40	5.32 - 5.52
Mr	5.88	5.78 - 5.98
Fe	6.40	6.30 - 6.50
Ni	7.46	7.36 - 7.56
BK	-	9.30 - 9.50
BK	-	11.50-11.90
PL	12.16	11.96-12.36
BK	-	12.46-12.86

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* Lines listed for elements are K_α; otherwise, BK - background intensity; EB - extraneous background (not normally used due to interference of pulse pileup from Si_{K_α}); PL - pulser.

TABLE II

	WDS			EDS						
	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO	MnO	FeO	SUM
Glass 1*	1.18	1.93	11.25	72.69	1.78	2.97	0.45	0.08	4.55	96.88
Anal.	1.2	1.8	11.5	75	2.0	2.7	0.5	0.09	4.75	99.54
Glass 2*	1.19	1.58	13.66	77.26	2.11	2.80	0.58	0.06	2.71	101.95
Anal.	1.2	1.8	13.5	75	2.0	2.7	0.5	0.09	2.85	99.64
Glass 3*	2.04	2.32	16.51	67.61	3.14	3.41	0.71	0.14	7.3	103.18
Anal.	1.68	2.5	16.1	65	2.8	3.78	0.7	0.12	6.8	99.48
Melt 1**	4.92	5.71	18.89	53.67	0.24	11.44	1.06	0.46	7.90	104.29
Melt 2**	4.70	7.21	17.93	52.48	0.41	11.07	1.23	0.41	7.66	103.10
Anal.[†]	3.38	7.05	17.5	50.1	0.49	9.4	1.3	0.16	9.8	99.18

*Measured against another Corning Glass Standard
**Inhomogeneous basalt melts measured against Corning Glass 3
†Average of 3 bulk analyses of crushed basalt

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